

## English Translation of JP 02-98932

(19) Japanese Patent Office (JP)

(12) Laid-open Disclosure Public Patent Bulletin (A)

(11) Patent Application Laid-open Disclosure Number: Hei 02-98932

(43) Laid-open Disclosure Date: April 11, 1990

(51) Int. Cl. <sup>5</sup>	Identification Code	FI
H 01 L 21/ 316	X	6824-5F
C 23 C 16/40		8722-4K

Request for Examination: Made

Number of Claims: 2 (6 pages in total)

(54) Title of the Invention:

METHOD FOR MANUFACTURING SILICON OXIDE FILM

(21) Application Number: Sho 63-252551

(22) Application Date: October 5, 1988

(72) Inventor: Yutaka HAYASHI

c/o Agency of Industrial Science and Technology Electrotechnical  
Laboratory  
1-1-4 Umezono, Tsukuba-shi, Ibaraki

(72) Inventor: Mitsuyuki YAMANAKA

c/o Agency of Industrial Science and Technology Electrotechnical  
Laboratory  
1-1-4 Umezono, Tsukuba-shi, Ibaraki

(72) Inventor: Takashi YOSHIMI

c/o Taiyo Yuden Co., Ltd.  
6-16-20 Ueno Taito-ku, Tokyo

(71) Applicant: Secretary of Agency of Industrial Science and Technology  
Electrotechnical Laboratory  
1-3-1 Kasumigaseki, Chiyoda-ku, Tokyo

(71) Applicant: Taiyo Yuden Co., Ltd.  
6-16-20 Ueno Taito-ku, Tokyo

(71) Applicant: Shin-Etsu Chemical Co., Ltd.

**English Translation of JP 02-98932**

**2-6-1 Ote-machi, Chiyoda-ku, Tokyo**

**To be continued to the last page**

## SPECIFICATION

### 1. Title of the Invention

#### METHOD FOR MANUFACTURING SILICON OXIDE FILM

### 2. Scope of Claim

(1) A method for manufacturing a silicon oxide film forming a glow discharge zone in a vacuum vessel and introducing organosilane and oxide gas or organosilane and non-metal oxide gas to form a silicon oxide film on a substrate, wherein component ratio of oxygen atoms to silicon atoms in said mixed gas composed of organosilane and oxide gas or organosilane and non-metal oxide gas is 100 or larger, wherein said mixed gas is introduced into said vacuum vessel.

(2) A method for manufacturing a silicon oxide film according to Claim 1, wherein said substrate temperature is heated to 330°C or higher.

### 3. Detailed Description of the Invention

#### [Industrial Field of the Invention]

The present invention relates to a method for manufacturing a silicon oxide film. More specifically, this invention relates to a method for manufacturing a silicon oxide film by plasma CVD using organosilane and oxygen gas or organosilane and non-metal oxide gas.

#### [Related Art]

So far, silicon oxide films used for a gate insulating film and a passivation film of a thin film transistor and the like are formed by so-called CVD using silane gas and non-metal oxide gas. For example, a glow discharge zone is formed in a vacuum vessel to which mixed gas composed of monosilane gas and laughter gas (dinitrogen monoxide) is introduced, and a silicon oxide film is deposited on a substrate.

#### [Problem to be Solved by the present Invention]

Required Characteristics of this kind of silicon oxide film used for the aforementioned gate insulating film, passivation film and the like of the thin film transistor are (1) low withstand voltage, (2) weak hysteresis characteristics of polarization or the like, (3) small accumulation of charge, (4) low refractive index, and so on.

## English Translation of JP 02-98932

However, a silicon oxide film deposited by conventional plasma CVD using organosilane and non-metal oxide gas has not been able to satisfy the required characteristics of the silicon oxide film to be used as the gate insulating film and the like of the thin film transistor. That is mainly because hydrocarbon group and hydroxyl group which are generated in reaction-growth of a silicon oxide film remain in the silicon oxide film.

That is, refractive index increases of the silicon oxide film when the hydrocarbon group remains in the silicon oxide film. In addition, in the case that hydroxyl remains in the silicon oxide film, there arises a problem such as decrease in withstand voltage, increase in hysteresis characteristics of polarization or the like, and increase in charge accumulation.

In consideration of the problem so far, an object of the present invention is to provide a method for manufacturing the silicon oxide film which can solve the problem.

[Means for Solving the Problem]

That is, a main point of a first means adapted for achieving the object of the present invention is a method for manufacturing a silicon oxide film forming a glow discharge zone in a vacuum vessel and introducing organosilane and oxide gas or organosilane and non-metal oxide gas to form a silicon oxide film on a substrate, wherein component ratio of oxygen atoms to silicon atoms in the mixed gas composed of organosilane and oxide gas or organosilane and non-metal oxide gas is 100 or larger, wherein the mixed gas is introduced into the vacuum vessel.

In addition, a main point of a second means is heating the substrate to at least 330°C in the method for manufacturing a silicon oxide film.

[Operation of the Invention]

FIG. 1 is a graph showing an example of the relationship between a composition ratio of oxygen atoms to silicon atoms in the mixed gas which is introduced into a vacuum vessel and ratio of hydrocarbon group remaining in a deposited silicon oxide film to Si-O group ( $\alpha_{\text{Si-CH}_3} / \alpha_{\text{Si-O}}$ ). In addition, the graph shows an example of the relationship between the component ratio above and refractive index. The present invention put emphasis on a fact shown by the graph.

## English Translation of JP 02-98932

That is, in the case of forming a silicon oxide film by CVD using organosilane and oxygen gas or organosilane and non-metal oxide gas, as shown with a solid line of FIG. 1, the composition ratio of hydrocarbon to Si-O group which remain in the deposited silicon oxide film is varied in making a change in the component ratio of oxygen atoms to silicon atoms in the mixed gas which is introduced into a vacuum vessel. As is clear from this graph, in the case where the component ratio of oxygen atoms to silicon atoms in the mixed gas is less than 100, hydrocarbon group remains in the deposited silicon oxide film. In addition, the ratio of hydrocarbon group to Si-O group decreases rapidly as the above ratio of the oxygen atoms increases. Moreover, when the composition ratio of oxygen atoms to silicon atoms reaches 100 and increases furthermore, the hydrocarbon group remaining in the silicon oxide film disappears from the film.

In addition, a region where the hydrocarbon group remains in the silicon oxide film, that is, a region where the component ratio of oxide atoms to silicon atoms is less than 100 to 1, the refractive index of the deposited silicon oxide decreases as the composition ratio of oxygen to silicon increases as indicated with a dotted line. When the component ratio of oxygen atoms to silicon atoms reaches 100, the refractive index becomes approximately 1.46 and stays flat even though the component ratio of oxygen increases 100 or more. Accordingly, like the first means of the present invention, by keeping the component ratio of oxygen atoms to silicon atoms in the mixed gas to be at least 100 to 1, the hydrocarbon group in the deposited silicon oxide film is decreased, and the refractive index is maintained at lowest value.

Next, FIG. 2 is a graph showing a relationship between a ratio of hydroxyl group remaining in a silicon oxide film of a deposited silicon oxide film to Si-O group and a substrate temperature ( $\alpha_{O-H}/\alpha_{Si-O}$ ) with a solid line, a relationship between the substrate temperature and an interface state amount of the silicon oxide film ( $N_{it}$ ) with a dotted line, a relationship between the substrate temperature and hysteresis of the silicon oxide film with a chain line, a relationship between the substrate temperature and withstand voltage of the silicon oxide film with a chain double-dashed line respectively in the case where a silicon oxide film is formed by CVD using organosilane and oxygen gas or organosilane and non-metal oxide gas. Besides, the substrate temperature is shown by a unit /K.

## English Translation of JP 02-98932

As shown in FIG. 2, in a region where the substrate temperature is less than 330°C ( $1/T = 1.66 \times 10^{-3}$ ), hydroxyl group remaining in the deposited silicon oxide film gradually decreases as the substrate temperature increases, and the hydroxyl group is disappears when the substrate temperature is at least 330°C. In addition, in the case where the substrate temperature is less than 330°C, an interface state amount ( $N_{it}$ ) and a hysteresis amount of the silicon oxide film decreases rapidly as the substrate temperature increases, and these values stay low when the substrate temperature is 330°C or higher. In addition, when the substrate temperature is not higher than 330°C, the withstand voltage of the silicon oxide film rapidly increases, and the withstand voltage reaches  $3 \times 10^6$  V/cm to be saturated. The present invention put emphasis on this fact, and proposes that a substrate temperature be at least 330°C when a silicon oxide film is deposited.

## [Detailed Description of the Preferred Embodiments]

Next, the embodiments of the present invention are described in detail with reference to FIG. 3.

## (Embodiment 1)

A silicon substrate 1 is cleansed by organic cleaning, a silicon oxide film on its surface is removed by 1 % hydrogen fluoride. After the silicon oxide film is rinsed with pure water, the water is removed by nitrogen blow. The silicon substrate 1 is then secured to a substrate holder 2 in a plasma CVD apparatus shown in FIG. 3. Besides decreasing pressure of a vacuum vessel 1 by an exhauster 4, the substrate 1 is heated to 350°C by a substrate heater 6. Laughter gas is supplied from a laughter gas introducing system 5b at a flow rate of 450 sccm, and monomethylsilane gas is supplied from a monomethylsilane gas introducing system 5a at a flow rate of 1.5 sccm, respectively. After these gases are mixed in a gas-blending machine 5c, the mixed gas is introduced into the vacuum vessel 1. Accordingly, ratio of oxygen atoms to silicon atoms of the mixed gas in the vacuum vessel 1 is 300, which is regulated by the steps above. Pressure of the vacuum vessel 1 is 1 Torr at this time.

By an RF power source 3, 13.56 MHz RF electric power is applied to parallel plate electrodes of 200 mmφ diameter, 25mm interval so as that difference between a traveling wave and a reflected wave becomes 15 W, and glow discharge is produced. A silicon

## English Translation of JP 02-98932

oxide film is then deposited by plasma CVD on the silicon substrate 1. When the silicon oxide film becomes 1000 angstrom thick, the power supply from the RF power source 3 is stopped; the substrate 1 is taken out after cooling down the temperature of the substrate 1 to a room temperature with keeping the vacuum vessel 1 vacuum.

Infrared absorption of the silicon oxide film thus obtained is measured, and a remaining hydrocarbon amount group in the film is then measured 0 as ratio to Si-O group. In addition, refractive index is measured 1.46 by ellipso film thickness meter.

For comparison, a flow rate of laughter gas is changed in a range of 0 to 600 sccm with maintaining a constant flow rate of monomethylsilane gas to 1.5 sccm, and composition ratio of oxygen atoms to silicon atoms is changed in a range from 0 to 400, each silicon oxide film is formed on the silicon substrate 1. An amount of remaining hydrocarbon group in thus obtained silicon thin film and refractive index of the film are measured.

FIG. 1 shows this result with relationship with the ratio of oxygen atoms to silicon atoms in the mixed gas. That is, in FIG. 1, a vertical axis represents the ratio of hydrocarbon group amount contained in the silicon oxide film to Si-O group amount and the refractive index, and a horizontal axis represents the composition ratio of oxygen atoms to silicon atoms in the mixed gas composed by monomethylsilane and laughter gas. As described before, by setting the component ratio of oxygen atoms to silicon atoms 100 or larger, it becomes possible to make hydrocarbon group remaining in the silicon oxide film almost 0. Also, refractive index of the silicon oxide film can be maintained at lowest value of 1.46.

(Embodiment 2)

Infrared absorption of the silicon oxide film obtained in the same manner as Embodiment 1 above, amount of hydroxyl group in the film is obtained as a ratio with an amount of Si-O group. In addition, by vacuum deposition, a dot electrode including Ni film of 500 angstrom film thickness is formed to compose a MOS structure, and a withstand voltage between a substrate and the dot electrode is measured. Moreover, by using the MOS structure, an interface state amount and magnitude of hysteresis of CV characteristics are measured, the withstand voltage is  $1.0 \times 10^6$  V/cm, the interface state

## English Translation of JP 02-98932

amount (Nrb) is  $3.5 \times 10^{11}$ , and the hysteresis amount is 0.

For comparison, the substrate temperature is changed in a range from 200°C to 400°C, and each silicon oxide film is formed on the silicon substrate 1 in the same manner. In the same manner as above, ratio of hydroxyl group amount in the film to Si-O group amount, the withstand voltage of the film, the interface state amount and hysteresis of CV characteristics are measured respectively.

This result is shown in FIG. 2. In FIG.2, a vertical axis represents the withstand voltage, the interface state amount and the hysteresis of the CV characteristics, and a horizontal axis represents the substrate temperature by using  $1/T$  (/ K). As described above, by setting a substrate temperature at least 330°C ( $1/T = 1.66 \times 10^{-3}$ ), it becomes possible to make hydroxyl group amount remaining in the silicon oxide film almost 0. Also, an increase in the withstand voltage and a decrease in the interface state amount and the CV characteristics becomes possible.

Note that the materials, the conditions and so on in each of the embodiments are an example. Accordingly, it is possible to carry out the present invention even if the materials, conditions and so on are changed. Major examples of the change are described below.

(a) In the embodiments above, monomethylsilane is used as organosilane; however, the same result is obtained when dimethylsilane, trimethylsilane and tetramethylsilane or the organosilane containing other alkyl instead of methyl is used instead of the organosilane. However, in the case that the organosilane is not gas, gasifying the organosilane or nebulizing to mix with non-metal oxide gas is required.

(b) In the embodiments above, laughter gas is used as non-metal oxide gas; however, the same result is obtained when  $O_x$  gas such as oxygen,  $HO_x$  gas such as vapor,  $CO_x$  such as carbon and the like is used.

(c) In the embodiments above, a plasma CVD device having a parallel plate shape is used; however, the same result is obtained when another type of a device which can resolve the non-metal oxide gas and organosilane by glow discharge is used.



## English Translation of JP 02-98932

(d) Appropriate change in deposition conditions such as deposition pressure, an RF power amount, an RF frequency, entire current rate of non-metal oxide gas and organosilane and area and intervals of electrodes does not ruin the operation and the effect of the present invention under a condition that the non-metal oxide gas and the organosilane are resolved by glow discharge.

[Effect of the Invention]

As described above, according to the present invention, a silicon oxide film having high withstand voltage, hysteresis characteristics of polarization or the like, small charge accumulation is obtained. Accordingly, a silicon oxide film having required characteristics to be used for an insulating film, a passivation film and the like of a thin film transistor can be manufactured by plasma CVD using organosilane and oxygen gas or organosilane and non-metal oxide gas.

#### 4. Brief Description of the Drawings

FIG. 1 is a graph showing an amount of hydrocarbon group contained in a film and refractive index in relation to composition ratio of oxygen atoms to silicon atoms in mixed gas composing organosilane and non-metal oxide gas.

FIG. 2 is a graph showing withstand voltage, an interface state amount and magnitude of hysteresis of CV characteristics in relation to a substrate temperature.

FIG. 3 is a view schematically showing plasma CVD device used in embodiments of the present invention.

In FIG. 1, reference numeral 1 denotes a vacuum vessel; 2, a substrate holder; 3, an RF power source; 4, an exhaustor; 5a, a monomethylsilane introducing system; 5b, a laughter gas introducing system; 5c, a gas-blending machine; 6, a substrate heater.

Applicant: Secretary of Agency of Industrial Science and Technology  
Electrotechnical Laboratory

English Translation of JP 02-98932

Applicant: Taiyo Yuden Co., Ltd.

Applicant: Shin-Etsu Chemical Co., Ltd.

Continued from the front page

(72) Inventor: Hideyo IDA

c/o Taiyo Yuden Co., Ltd.

6-16-20 Ueno Taito-ku, Tokyo

(72) Inventor: Kiyohiro KONDO

c/o Shin-Etsu Chemical Co., Ltd.

2-6-1 Ote-machi, Chiyoda-ku, Tokyo

(72) Inventor: Satoshi OKAZAKI

c/o Advanced Functional Materials Research Center

2-13-1 Isobe, Anaka-shi, Gunma